D. Processing and Characterization of Structural and Functional Materials for Heavy Vehicle Applications

J. Sankar, Z. Xu, and S. Yarmolenko
North Carolina A & T State University
1601 East Market Street
Greensboro, NC 27411
(336) 256-1151, extension 2282; fax: (336) 256-1153; e-mail: sankar@ncat.edu

DOE Technology Development Area Specialist: Dr. Sidney Diamond
(202) 586-8032; fax: (202) 586-2476; e-mail: sid.diamond@ee.doe.gov
ORNL Technical Advisor: D. Ray Johnson
(865) 576-6832; fax: (865) 574-6098; e-mail: johnsondr@ornl.gov

---

Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No:DE-AC05-00OR22725
Subcontractor: North Carolina A&T State University, Greensboro, North Carolina

---

Objectives

- Produce yttria-stabilized zirconia (YSZ) thin films using a combustion chemical vapor deposition (CCVD) technique for solid oxide fuel cells (SOFCs).
- Investigate the nucleation of YSZ and its controlling parameters.
- Study the thin film microstructure evolution.
- Enhance the film deposition rate.

Approach

- Deposit YSZ thin films using a CCVD technique.
- Characterize the films using scanning electron microscopy (SEM) and X-ray diffraction (XRD).
- Study the effects of substrate temperature and metal concentration on the nucleation density.
- Examine the thin film microstructure evolution by experiment and stochastic simulation.
- Optimize the operation parameters of the CCVD system.

Accomplishments

- Enhanced the nucleation density.
- Developed a stochastic model to simulate the thin film microstructure evolution.
- Established a set of conditions for high film growth rates.

Future Direction

- Study YSZ film deposition on porous electrodes.

Introduction

YSZ, a material that conducts oxygen ions, has conventionally been used as an electrolyte in SOFCs and in oxygen sensors for pollution and safety monitoring, control and automation of industrial processes, and energy conservation.[1] Because of the relatively low electrical conductivity of the YSZ material (about 0.1 $S \cdot cm^{-1}$ at 1000°C), most of the ohmic loss is due to the resistance of the electrolyte. To reduce the ohmic loss and increase the power-generating efficiency of a fuel cell, it is desirable to use a thin film electrolyte. On the other hand, temperatures as high as 1000°C are usually employed with YSZ to obtain a satisfactory level of ionic conductivity. The need for high temperatures makes material selection difficult and increases the product cost greatly. Reducing the thickness of the electrolyte would increase the ionic conductivity at lower temperatures.

YSZ thin films have usually been synthesized by chemical vapor deposition (CVD) or electrochemical vapor deposition (EVD).[2–5] However, the vacuum systems used in these techniques require the use of a vacuum chamber, which limits the sizes of the parts that can be coated and increase production costs. A technique called liquid fuel CCVD is a promising alternative for producing YSZ thin films for industrial applications. CCVD works in the open atmosphere and offers the potential for conformal deposition of films on non-flat surfaces. Because no vacuum chamber is needed for the process, the film can be deposited on parts of any size. The precursor concentration in liquid fuel is relatively high compared with that usually used in low-pressure CVD processes; therefore, CCVD is expected to have a higher deposition rate. CCVD is a promising technique for producing YSZ thin films for industrial SOFC applications at a lower cost than other CVD/EVD techniques.

An SOFC requires that the electrolyte be highly dense to avoid any cross-flow of oxygen or fuel. The main purpose of this research is to produce dense YSZ thin films through the study of nucleation and microstructure evolution. Methods of enhancing the growth rate of YSZ are being studied because of the potential for reducing the cost of fuel cell manufacturing through the use of thin film technology.

Approach

Thin films of YSZ as an electrolyte for SOFCs have been deposited using CCVD. The deposition system was developed at North Carolina A&T State University. Metal-organic reagents were dissolved in organic solvent (toluene). The solution was mixed with oxygen and atomized into small aerosols with a nebulizer and then was ignited by a pilot flame. Thin films were deposited on substrates placed downstream of the aerosol flame.

A nucleation study of YSZ was performed by varying the substrate temperature and metal concentration in the solvent. At a designed condition, depositions were conducted for varying time periods. The microstructures of these depositions were observed and analyzed. The grain growth was studied with stochastic modeling. The efforts to enhance the film growth rate were carried out through studies of the effect of the thermophoresis and metal concentration. All the present depositions were performed on mirror-polished single-crystal silicon substrates. The phases of the deposited films were examined with XRD, and their morphology was characterized through SEM.

Results

Nucleation

Effect of substrate temperature. The temperature of the substrate is an important factor that controls nucleation density, defined as the number of aggregates created per unit of area. To be able to use the image

analysis software Image Pro to compute the nucleation density, the nucleation time of the YSZ particles was set for 130 seconds. The depositions were conducted at substrate temperatures of 800, 900, 1000, 1100, and 1200ºC and a metal concentration of 1.25E-03 M. The as-grown samples were characterized with SEM as shown in Figure 1.

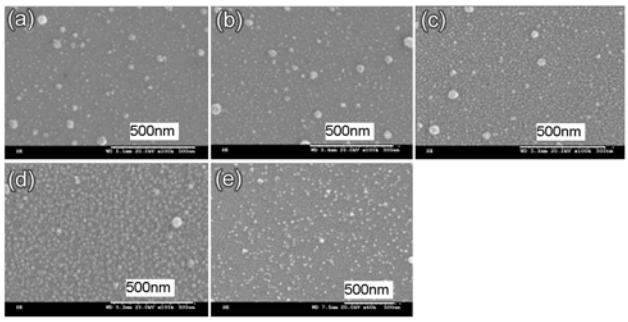

Figure 1. Micrographs of YSZ nuclei nucleated at substrate temperatures (a) 800ºC, (b) 900ºC, (c) 1000ºC, (d) 1100ºC and (e) 1200ºC at a nucleation time of 130 seconds and a total metal concentration of 1.25×10^{13} M.

Using the analysis software to count the particle number in the specific area, it was found that the nucleation rates ranged over an order of magnitude, from 10^{10} to 10^{11} cm^{-2} in the tested temperature range. The nucleation rate variation versus the substrate temperature is illustrated in Figure 2. It is obvious that the tendency of the nucleation rate versus the substrate temperature can be divided into two sections. With the substrate temperature between 1000 and 1200ºC, the nucleation rate decreases with the substrate temperature; in the substrate temperature range of 800 to 1000ºC, the nucleation rate increases with substrate temperature. The former nucleation rate tendency was well accepted. As far as we know, the latter tendency has not been reported. It is proposed that at low substrate temperatures, the material species in the gas phase condense into the solid phase and coagulate into particles. They rebound from the surface instead of becoming adsorbed when they

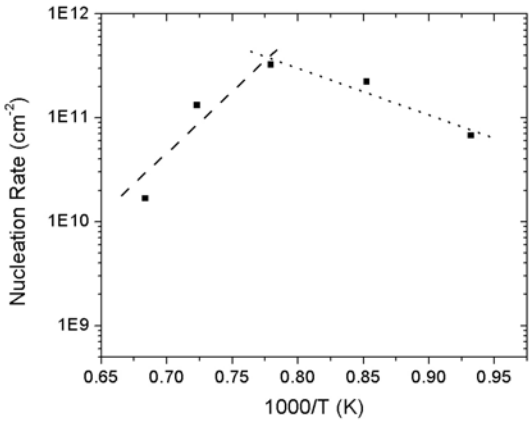

Figure 2. YSZ nucleation rate as a function of the substrate temperature, according to the information in Figure 1.

hit the substrate surface. This process also leads to depletion of species in the gas phase that is needed for CVD and then partially results in a decrease in the nucleation rate. The images in Figure 1 also reveal that, on the samples nucleated at the low temperatures, there are many large nodular particles that support our conclusions.

Effect of metal concentration. Another method of enhancing the nucleation rate was to increase to deposition flux, i.e., the metal concentration, for our experimental system. At the low concentrations of 5×10^{-4} and 1.25×10^{-3}, only isolated particles presented on the substrate surface after depositions of 130 seconds, whereas almost continuous films were obtained when the concentration was increased to 3×10^{-3} M and up. At the high total metal concentrations, the particle size reached up to 30–50 nm. From this set of experiments, it can be concluded that the lowest metal concentration, 5.5×10^{-4}M, is not suitable if a high nucleation rate is demanded.

Structural Evolution

Experimental study. To grasp the physics of the evolution process of the YSZ thin film, the grain sizes at various stages of

the processing time were measured for statistical post-processing. Figure 3 shows the micrographs of YSZ particles/crystallites at different processing times. In Figure 3(a), the nuclei can hardly be seen after only 70-second processing, except some large particles that are assumed to be contamination. From Figures 3(b) to (d), with the increase in processing time, the size of the particles is increased; however, the number of particles is reduced. This phenomenon can be interpreted by the mechanisms of coarsening and coalescence of the growing particles. With increased time of processing, the sizes of the particles increase. Some secondary nucleation and growth on the large particles can be noticed. It is also reasonable to assume that the secondary nucleation should take place on the substrate before all the surface of the substrate is covered with particles. The film consists of both (111) and (100) oriented crystals. The difference in orientation originated at the stage when the sizes of particles were very small.

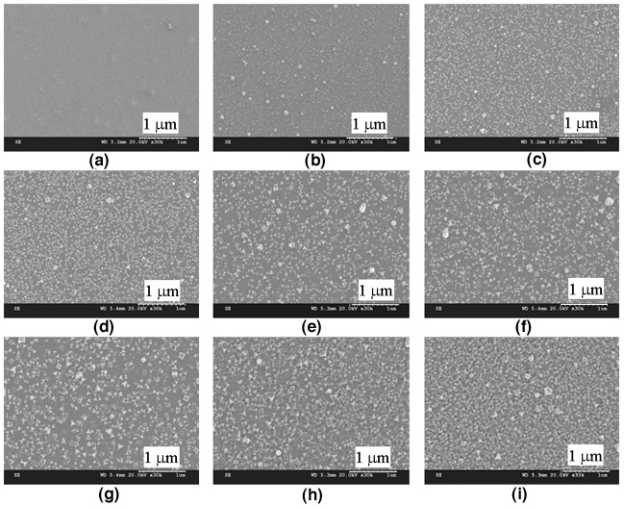

Figure 3. Microstructure of the YSZ particles/crystallites at different processing times: (a) 70, (b) 130, (c) 190, (d) 250, (e) 310, (f) 370, (g) 430, (h) 490, and (i) 550 seconds on Si(100) substrates, at a substrate temperature of about 1200ºC and a metal concentration of 1.25×10^{-3} M.

According to the obtained mean particle radii, particle growth rate can be estimated by plotting the mean diameter versus the growing time, as shown in Figure 4. The particle growth rate is approximately linear during the time period studied (130 to 430 seconds). The intercept of the line on the time axis is about 33.3 seconds, which shows the incubation time for nucleation. With a prolonged deposition time, a continuous thin film can be obtained.

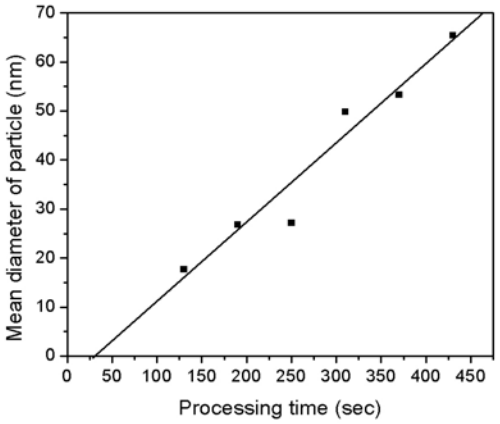

Figure 4. Particle growth rate vs. processing time, based on the data obtained from the micrographs, as shown in Figure 3.

Stochastic simulation. The number and sizes of the particles were obtained by using the image processing software. After statistical post-processing, a comparison of cumulative distribution functions (CDFs) of grain radius normalized by the mean radii is given in Figure 5. As can be seen from Figure 5, there is a distinct dispersion among these CDFs plotted in the normalized space. Thus the use of a normal grain growth model cannot accurately capture the evolution process of grains in YSZ thin films. The deviation from the normal grain growth model is attributed mainly to the orientation-dependent grain boundary energies and mobility.

The lognormal distribution has been used extensively as the initial distribution of grain size.[6,7] To validate the use of the lognormal

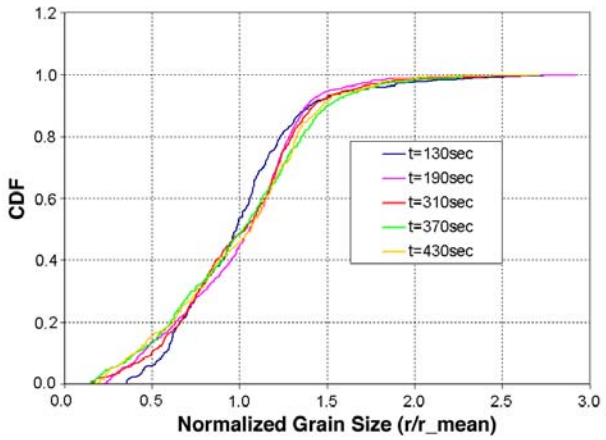

Figure 5. Comparison of CDFs of grain radius in normalized space.

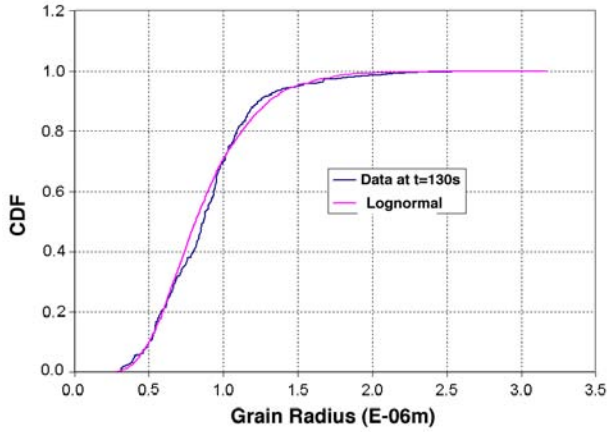

Figure 6. Illustration of the accuracy of using an equivalent lognormal distribution for statistical characterization of initial grain size distribution.

model, a comparison of the initial CDF of grain radius at *t=130 s* with its equivalent lognormal distribution is shown in Figure 6. As shown in Figure 6, the equivalent lognormal distribution can accurately capture the true initial grain size distribution. A stochastic model was developed by taking the radii of the neighboring grains and the orientation-dependent constants into consideration. The computational efforts were greatly reduced by dividing the entire population of grains into several sub-groups based on the level of their percentiles. It was assumed that all grains within each sub-group have an identical behavior of grain growth. The orientation-dependent grain growth constants were determined from curve fitting of the experimental data. An example of comparing model prediction with the experimental observations is shown in Figure 7.

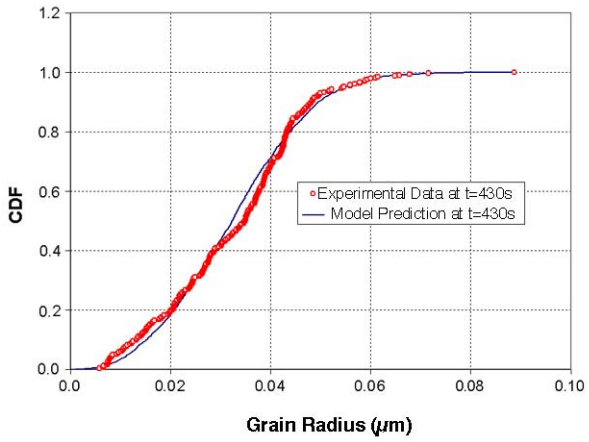

Figure 7. Comparison of model prediction with measured CDF data of grain radius at *t = 430 s*.

Growth Rate

Thermophoresis is a thermal-gradient–directed flow of material from high-temperature regions to low-temperature regions. Thermophoresis had been found to be a strong factor in some CVD environments.[8] A temperature gradient across a diffusion boundary layer causes a thermophoresis effect. In our case, if the flame were hotter than the substrate, on average, the gas molecules from the substrate would have a smaller velocity than the gas molecules traveling toward the substrate. This situation creates a driving force for YSZ clusters formed in the direction toward the substrate. A larger temperature gradient adjacent to the substrate increases the thermophoresis effect. The study of the effect of thermophoresis was carried out by film depositions at different substrate-to-nuzzle distances from 51 mm (far into the flame) to 83 mm (out of the visible end of the flame). The film thickness measured on SEM images is plotted versus the substrate-to-nozzle

distance in Figure 8 (solid line). The data can be fit by an exponential equation. With the increase of the substrate-to-nozzle distance, the precursor concentration in the flame will be attenuated because of the expansion of the flame. Normalization was done to eliminate the effect of concentration dilution on the film growth rate. The normalized thickness data were again plotted in the same graph of the originally measured data, as shown in curve 2 of Figure 8, the dashed line. It is apparently noticeable that after normalization, the growth rate of the film still follows the exponentially decaying mode with the substrate-to-nozzle distance. In other words, the parameter substrate-to-nozzle distance does play a role in film growth.

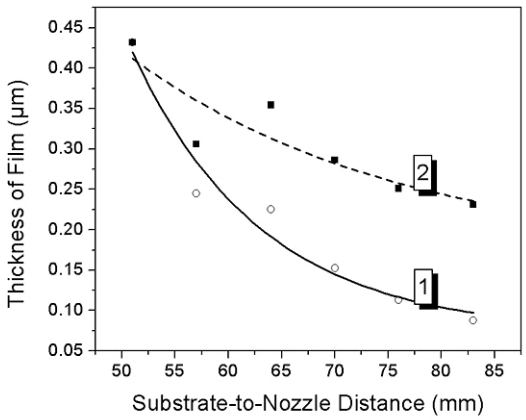

Figure 8. Film thickness as a function of the substrate-to-nozzle distance, line (1) for the original measured data, line (2) for the normalized data.

The effect of the metal concentration on the film growth rate is shown in Figure 9. Within the range of the concentration employed in our experiments, a linear relationship was obtained between the film growth rate and the concentration. Based on observing the morphologies of the samples, the films had well-crystallized and faceted particles as long as the metal concentrations were less than 4.25×10^{-3} M. Beyond this limitation, the film was in a cauliflower-like structure.

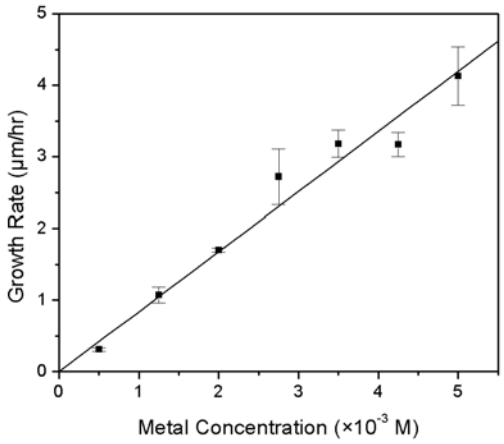

Figure 9. Film growth rate versus metal concentration in the liquid solution.

Conclusions

According to the investigations we have conducted, the CCVD technique has been demonstrated to be a promising method for film processing of YSZ electrolyte. Nucleation density can be improved by controlling the substrate temperature and the metal concentration appropriately. The analysis of the grain growth demonstrated that after the initial stage, the grain growth does not follow the lognormal mode. A stochastic model has been developed to predict the grain size in the film at any deposition time. The experiments confirmed the enhancement of the film growth rates by employing the effect of the thermophoresis and increasing the metal concentration.

References

1. S. P. S. Badwal, "Ceramic Superionic Conductors," Chapter 11 in *Materials Sciences and Technology, A Comprehensive Treatment*, Ed. R. W. Cahn, P. Haasen, E. J. Kramer, Vol. 11, p. 570, 1994.

2. G. Garcia, J. Casado, J. Llibre, and A. Figueras, *J. Crystal Growth*, **156**, 426 (1995).

3. S-C. Hwang and H-S. Shin, *J. Am. Ceram. Soc.*, **82**(10), 2913 (1999).

4. U. B. Pal, and S C. Singhal, *J. Electrochem. Soc.*, **137**, 937 (1990).

5. L. G. J. De Haart, Y. S. Lin, K. J. de Vries, A. J. Burggraaf, *J. Eur. Ceram. Soc.*, **8**(1), 59 (1991).

6. V. Y. Novikov, *Acta Mater.* **47**(18), 4507 (1999)

7. C. V. Thompson, *Annu. Rev. Mater. Sci.* **20**, 245 (1990).

8. W. Bai, K. L. Choy, N. H. J. Stelzer, and J. Schoonman, *Solid State Ionics*, **116**, 225.

Publications

Z. Xu, J. Sankar, S. Yarmorlenko, "Yttria-stabilized Zirconia Coatings Produced Using Combustion Chemical Deposition," *Surface and Coating Tech.*, in press, 2003.

Z. Xu, C. Hilton, B. Watkins, S. Yarmolenko, and J. Sankar, "Thin YSZ Electrolyte Film Depositions on Dense and Porous Substrates," paper IMECE2003-43330 in *2003 ASME International Mechanical Engineering Congress and RD&D Expo*.

Z. Xu, J. Sankar, S. Yarmolenko, Q. Wei, "Nucleation And Growth of Yttria-Stabilized Zirconia Thin Films Using Combustion Chemical Vapor Deposition," *Materials Research Society Symposium Proceedings*, Vol. 756, pp. 509–514 (2003).

Z. Xu, S. Yarmolenko, J. Sankar, "Enhancement Of YSZ Thin Film Deposition Rate In CCVD," pp. 862–862 in *Proceedings of 10th International Conference on Composites Engineering*, New Orleans, Louisiana, July 20–26, 2003.